Graphical Abstract

Synthesis, crystal structure, magnetic properties and second harmonic generation of a new noncentrosymmetric coordination compound: triaqua(4-amino-6-methoxypyrimidine) cuprate(II) sulfate

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The Cu(II) cation is five-coordinated by two nitrogen atoms of the 4-amino-6-methoxypyrimidine ligand and three water oxygen atoms. The ligand molecules and the 5-connected Cu centers link each other to give a 1-D corrugated hybrid chain running along the *b*-axis direction.

Original article

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ABSTRACT

The chemical preparation, crystal structure and infrared spectroscopic characterization of the triaqua(4-amino-6-methoxypyrimidine) cuprate(II) sulfate, $[\text{Cu}(\text{C}_5\text{H}_7\text{N}_3)(\text{H}_2\text{O})_3]\text{SO}_4$, is reported. The compound crystallizes in the noncentrosymmetric orthorhombic space group $P2_12_12_1$ with lattice parameters $a = 7.9025$ (3), $b = 11.1189$ (4), $c = 12.9720$ (4) Å, $V = 1139.81$ (7) Å³ and $Z = 4$. The Cu(II) cation is five-coordinated, in an early half-way between square pyramidal and trigonal bipyramidal fashion, by two nitrogen atoms of the 4-amino-6-methoxypyrimidine ligand and three water oxygen atoms. In the atomic arrangement, the organic ligands and the 5-connected Cu centers are linked with each other to give a 1-D corrugated hybrid chain running along the b -axis direction. The chains are interconnected by the SO_4^{2-} anions via $\text{O}—\text{H}\cdots\text{O}$, $\text{O}—\text{H}\cdots\text{S}$, $\text{C}—\text{H}\cdots\text{O}$ and $\text{N}—\text{H}\cdots\text{O}$ hydrogen bonds to form layers spreading parallel to the (011) plane. The vibrational absorption bands were identified by infrared spectroscopy. Quantitative measurements of the second harmonic generation (SHG) of a powdered sample at 1064 nm were performed and a relative efficiency of 5.2 times the KDP standard was observed. Magnetic properties were also defined to characterize the complex.

1. Introduction

Transition-metal complexes have been proven to be useful for the design of molecular ferromagnets, as catalysts for many organic reactions, as models for the active sites in metalloenzymes, as optical and luminescent materials, or as DNA cleavage reagents [1–5]. Furthermore, the complexes containing transition metals may be formed by bridging ligands that can mediate magnetic interactions between paramagnetic metal ions [6]. Among these materials, copper(II) complexes have been found to have the potential for treatment of cancers and many other disease [7]. They draw great attentions due to their high nucleolytic efficiency [8, 9]. They can break the DNA chains in the presence of H_2O_2 and reducing agents, and are used broadly as foot printing agents for proteins and DNAs [10], probes of the dimensions of the minor groove of duplex structures [11], and identifiers of transcription starting sites [12]. Copper(II) complexes have been probed electrochemically [13, 14] magnetically [15–19] and by EPR [20–21] for their electronic situation. The Cu(II) complexes have different molecular geometries, such as tetrahedral, square planar, square pyramidal and octahedral [22].

Recently, it has shown that it is possible to synthesize coordination compounds, with fascinating structures and interesting physical properties, by combining transition metal ions with pyrimidine type ligands and several pseudohalide auxiliary spacers [23]. Here a new member of this family the 4-amino-6-methoxypyrimidine cuprate(II) sulfate trihydrate is presented, which has been obtained during our studies of the preparation of new coordination compounds with pyrimidine derivatives as ligands [24].

On other hand, in the past few years, inorganic-organic hybrid crystalline materials with interesting electrical, magnetic, and nonlinear optical (NLO) properties have attracted the attention of the material science community [25, 26]. In hybrid materials, the most usual provider of the magnetic properties is the inorganic part, whereas significant second-order NLO responses are more frequently originated from the organic counterpart. For this purpose, the essential requirement is a large molecular first-order hyperpolarizability β of the chromophore, typically obtained in planar conjugated π -electron systems, end capped with electron-donor and –acceptor moieties [27–33].

In addition to the molecular properties, it is also essential that the supramolecular organization of the chromophores maximizes the bulk electro-optic response, first of all crystallizing in noncentrosymmetric space groups and then optimizing the phase matching [34, 35].

In this paper, we present the synthesis, crystal structures, IR characterization, magnetic properties and second harmonic generation quantitative measurements of triaqua(4-amino-6-methoxypyrimidine) cuprate(II) sulfate, which is a chiral organic-inorganic network constructed by hydrogen bonds.

2. Experimental

Chemical preparation: A solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (22 mg, 0.1 mmol) in water was added dropwise to a solution of 4-amino-6-methoxypyrimidine (25 mg, 0.2 mmol) in ethanol (10 mL). After stirring for 30 min, the mixture was filtered. Crystals suitable for X-ray analysis were obtained after five days by evaporating the filtrate at room temperature (yield = 81%).

X-ray single crystal structural analysis: Single crystals were carefully selected under a microscope and mounted on a Mitegen micromesh mount with the help of a trace of mineral oil. X-ray diffraction data were collected at 100 K on a Bruker AXS D8 Quest CMOS diffractometer. Data were collected, the unit cell determined, and the data integrated and corrected for absorption and other systematic errors using the Apex2 suite of programs [36]. SHELXS-97 [37] was used to solve the structure using direct methods and SHELXL6.14 [38], SHELXL-2014 [39] and SHELXLE [40] were used for refinement. The crystal was found to be racemically twinned with a twin domain ratio of 0.872(8) to 0.188(8). The drawings were made with Diamond [41]. Crystal data and experimental parameters used for the intensity data collection are summarized in Table 1.

Infrared spectroscopy: The IR spectra were recorded in the range 4000–400 cm^{-1} with a “Perkin–Elmer FTIR” spectrophotometer 1000 using samples dispersed in spectroscopically pure KBr pressed into a pellet.

Magnetic properties: Magnetic measurements were carried out for a microcrystalline sample with random orientation on a SQUID (Quantum Design MPMS XL7) magnetometer down to 2 K. Temperature dependence of the dc susceptibility was measured under 500 Oe. The molar unit of the paramagnetic susceptibility χ_p was chosen as the quantity per one mole of $[\text{Cu}(\text{C}_5\text{H}_7\text{N}_3\text{O})(\text{H}_2\text{O})_3]\text{SO}_4$. The experimental raw data were corrected for the diamagnetic contribution, $-0.000173 \text{ emu mol}^{-1}$, which was estimated by the Pascal diamagnetism.

Kurtz-Perry powder method: The Second-Harmonic Generation (SHG) efficiency of the compound triaqua(4-amino-6-methoxypyrimidine) cuprate(II) sulfate was measured using the Kurtz and Perry powder method [42]. The measurements were performed at a wavelength of 1064 nm produced by a Nd:YAG laser operating at 10 Hz and producing 10 ns pulses with a pulse energy of 11 mJ. The sample preparation procedure was as follows: the material was milled to a fine powder and compacted in a mount and then installed in the sample holder. Sample grain sizes were not standardized. Signals between individual measurements were seen to vary in some cases by as much as $\pm 10\%$. For a proper comparison with the KDP reference material the measurements were averaged over several laser thermal cycles.

3. Results and discussion

3.1. X-ray diffraction study

The asymmetric unit of $[\text{Cu}(\text{C}_5\text{H}_7\text{N}_3)(\text{H}_2\text{O})_3]\text{SO}_4$ consists of one Cu(II) cation, one 4-amino-6-methylpyrimidine (L) ligand, three water molecules and one SO_4^{2-} anion (Fig. 1). The Cu(II) ion is pentacoordinated by the three water oxygen atoms and two nitrogen atoms (N1 and N2) of the monodentate L ligand to give a distorted square pyramidal coordination geometry. The geometry of penta-coordinated metal complex may conveniently be measured by the Addison parameter [43] (trigonality index, $\tau = (\beta - \alpha)/60$, where α and β are the two largest L-M-L angles of the coordination sphere), that is zero for an ideal square-pyramidal complex and one for a trigonal bi-pyramidal complex. In the title complex, the calculated τ values of the title compound is $\tau(\text{Cu}) = 0.42$, where β and α values are $176.55(6)^\circ$ and $151.17(5)^\circ$, respectively (Table S1 in Supporting information), indicating a distortion from the regular polyhedron nearly halfway between square pyramidal and trigonal bi-pyramidal. Two monodentate 4-amino-6-methoxypyrimidine ligands coordinate through N1 and N2 at equatorial positions with nearly identical Cu-N bond distances of 2.031(1) and 2.038(1) Å. The two remaining equatorial sites are occupied by the O2 and O3 water oxygen atoms with again very similar bond distances of 1.956(1) and 1.944(1) Å to the copper ion. The O4 water oxygen atom occupies the axial position and features a significantly longer Cu-O bond of 2.165(1) Å as is commonly observed for many Cu(II) complexes. The two 4-amino-6-methoxypyrimidine moieties are directed trans to each other at an angle of $151.17(5)^\circ$, representing the principal distortion from an ideal square pyramidal geometry, while there is only a small departure from linearity for the other trans angle O2-Cu-O3 [$176.55(6)^\circ$]. In the atomic arrangement, the L ligands and the 5-connected Cu centers link each other to give a 1-D corrugated hybrid chain running along the *b*-axis direction (Fig. 2). These chains, located at $z = 1/4$, are interconnected by the SO_4^{2-} anions via $\text{O}-\text{H}\cdots\text{O}$, $\text{O}-\text{H}\cdots\text{S}$, $\text{C}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds to form layers spreading parallel to the (011) plane (Fig. 2, Table S2 in Supporting information). These layers are located at $x = n/2$ and interconnected through $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds to form a three dimensional network (Fig. 3). Within the organic ligand 4-amino-6-methoxypyrimidine, an examination of the C-N bond distance of the NH_2 group (Table S3 in Supporting information), shows that C2-N3 [1.335 (2) Å] is short for C-N

single bond, but still not quite as contracted as one would expect for a fully established C=N double bond. This bond length feature is consistent with an imino resonance form as it is commonly found for C-N single bond involving sp² hybridized C and N atoms [44, 45]. Furthermore, the distance C5-O1 [1.439 (2) Å], clearly indicates a single bond, while the distance C4-O1 [1.333 (2) Å] is shorter which is probably due to the donor mesomeric effect of the methoxy group [46].

3.2. IR spectroscopy

FTIR spectroscopy was used to verify the functional groups present in the crystal and to investigate their vibrational behavior in the solid state. The characteristic vibrational modes of this compound can be compared to those of similar materials [47-49]. The very large band in the high-frequency region, spreading between 3600 cm⁻¹ and 2600 cm⁻¹, correspond to the stretching vibrations of the N-H, C-H and O-H groups interconnected by a system of hydrogen bonds in the crystal [50]. The band at 1655 cm⁻¹ is assigned to the O-H and N-H bending modes. The bands observed in the 1600 cm⁻¹ and 1050 cm⁻¹ region can be assigned to the valence vibrations of the C=C, C=N, C-C and C-N bonds [51]. The observed bands in the range 1000–600 cm⁻¹ can be assigned to the CH₃ and NH₂ groups and to the skeleton of amino-pyrimidine rings symmetric, asymmetric, stretching and deformation modes [52, 53].

3.3. Magnetic properties

This material will have a one-dimensional coordination polymer structure and will be regarded as an S = 1/2 one-dimensional magnetic system if superexchange interactions via the organic ligands work between copper ions. In order to investigate intensity and sign of the magnetic interactions in this material, magnetic studies were carried out. This material exhibited a paramagnetic behavior. Fig. 4a shows temperature dependence of the paramagnetic susceptibility of this material. The χ_p value showed a gradual increase, decreasing with temperature, and made a broad maximum at *ca.* 22 K. This magnetic behavior may be originated from the short-range magnetic ordering, which is characteristic of low dimensional magnetic materials. Below 5 K, the χ_p value again increases, decreasing with temperature. This behavior is due to Curie term from lattice defects or magnetic impurities. Fig. 4b shows temperature dependence of the product of the paramagnetic susceptibility and temperature. The $\chi_p T$ value at 300 K is 0.423 emu K mol⁻¹, and decreased, with decreasing in temperature monotonically. This fact suggests dominance of intermolecular antiferromagnetic interactions between copper atoms.

The magnetic behavior of this material can be interpreted in terms of the antiferromagnetic regular chain model using the Hamiltonian in eq 1, where J is the intrachain magnetic coupling constant between neighboring magnetic molecules i and j ,

$$H = -2J\hat{S}_i \times \hat{S}_j \quad (1)$$

The analytical expression for the paramagnetic susceptibility χ_{1D} is given as

$$C_p = \frac{C}{T} \frac{4(0.25 + 0.14995y + 0.30094y^2)}{1 + 1.9862y + 0.68854y^2 + 6.0626y^3} + \frac{C_{imp}}{T} \quad (2)$$

where $C = Ng^2\mu_B^2/(4k_B)$, $y = |J|/(k_B T)$. N , g , μ_B , and k_B are the Avogadro's number, the coordination number, the g factor, the Bohr magneton, and the Boltzmann constant, respectively [54, 55]. The solid curve in Figs.6a and 6b is the best fit with $g = 2.11$, $2J/k_B = -36$ K, and $C_{imp} = 0.0038$ emu Kmol⁻¹.

This material showed no magnetic ordering transition down to 2 K in spite of the magnetic coupling constant of -36 K. This indicates that this material has a one-dimensional magnetic character [55] because the coordination chains are well separated and magnetically isolated by water molecules or the anions between the neighbor chains. This material has a bridged structure of copper atoms via the pyrimidine ligands. Ishida et al. reported that detailed magnetic properties of a di-nuclear metal complex DPPM-Cu bridged via a pyrimidine ligand between two copper ions [56]. Their magnetic parameters were $g = 2.29$ and $2J/k_B = -46$ K. The magnetic coupling constant is inconsistent with our value.

3.4. Nonlinear optical response

To determine the NLO response of this new coordination compound we measured the SHG efficiency with the Kurtz-Perry method [40] using a polycrystalline sample. A good SHG efficiency of 5.2 times the KDP standard was observed. We plan, in the near future, to characterize further the second order nonlinear susceptibility using the Maker fringe technique.

4. Conclusion

We have developed new nonlinear optical triaqua(4-amino-6-methoxypyrimidine) cuprate(II) sulfate crystals, which show orthorhombic space group $P2_12_12_1$ symmetry. The coordination polyhedron around the central Cu(II) ion is about half way between square-pyramidal and trigonal-bipyramidal geometry. The organic ligands and the 5-connected Cu centers link each other to give a 1-D corrugated hybrid chain running along the b -axis. These chains are interconnected by the SO₄²⁻ anions via a set of hydrogen bonds to form layers spreading parallel to (011) plane. The vibrational absorption bands were identified by infrared spectroscopy. Intermolecular antiferromagnetic interactions between

copper atoms are expected to predominate in the compound. The crystals exhibit a good Second Harmonic Generation (SHG) efficiency of 5.2 times the potassium dihydrogen phosphate (KDP) standard.

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Fig. 1 A view of the asymmetric unit in the crystal structure of $[\text{Cu}(\text{C}_5\text{H}_7\text{N}_3)(\text{H}_2\text{O})_3]\text{SO}_4$ showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. The dotted lines indicate hydrogen bonds.

Fig. 2 View along the [011] direction of an inorganic-organic layer $[\text{Cu}(\text{C}_5\text{H}_7\text{N}_3)(\text{H}_2\text{O})_3]\text{SO}_4$. The dotted lines indicate hydrogen bonds.

Fig. 3 Projection along the c -axis of the crystal packing of the title compound. The dotted lines indicate hydrogen bonds.

Fig. 4 Temperature dependence of the molar magnetic susceptibility χ_p (a) and $\chi_p T$ (b) of $[\text{Cu}(\text{C}_5\text{H}_7\text{N}_3)(\text{H}_2\text{O})_3]\text{SO}_4$ for an external field of 500 Oe. The solid line corresponds to the best theoretical fit.

Table 1. Experimental details

<i>Crystal data</i>	
Chemical formula	$\text{C}_5\text{H}_{13}\text{CuN}_3\text{O}_4 \cdot \text{O}_4\text{S}$
M_r	338.78

Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	100
$a, b, c(\text{\AA})$	7.9025 (3), 11.1189 (4), 12.9720 (4)
$V(\text{\AA}^3)$	1139.81 (7)
Z	4
Radiation type	Mo $K\alpha$
μ (mm $^{-1}$)	2.14
Crystal size (mm)	0.35×0.23×0.22
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan, Apex2 v2014.1-1 (Bruker, 2014)
$T_{\min}, T_{\max}$	0.558, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12225, 4296, 4106
R_{int}	0.020
$(\sin \theta/\lambda)_{\max}$ ($\text{\AA}^{-1}$)	0.770
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.020, 0.048, 1.08
No. of reflections	4296
No. of parameters	189
No. of restraints	8
$\Delta\rho_{\max}, \Delta\rho_{\min}(\text{e \AA}^{-3})$	0.51, −0.35
Absolute structure	Refined as an inversion twin.
Absolute structure parameter	0.188(8)